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Influence of various parameters on the electrochemical treatment of landfill leachates

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Abstract

The influence of some basic parameters of an electrolytic system on the effectiveness of the treatment of landfill leachates is investigated. The controlling parameters of the system examined were: (i) the leachate input rate, (ii) pH and temperature, (iii) the amount of electrolyte (NaCl) added, (iv) the voltage applied and (v) the concentration of Fe^{2+} (added as $FeSO_4 \cdot 7H_2O$). The performance of the system was assessed in terms of the COD, BOD_5 and NH_4^+ reduction in the leachate samples as well as in terms of the energy consumption of the system (i.e., kWh consumed per kg of COD removed). These two parameters are referred to as the optimization parameters of the system. By implementing a 2^6 factorial experiment, linear models, which interrelate each optimization parameter with the controlling parameters of the system, were generated. Using these models, effective treatment of landfill leachates by electrochemical oxidation can be designed.

1. Introduction

There is a worldwide consensus among many experts that properly designed landfilling is the most cost effective, least polluting and safest means of disposing of solid urban waste [1]. However one of the major problems of this method is the collection and treatment of generated leachates. Untreated landfill leachates can permeate the ground and mix with surface waters, contributing to their pollution, and hence posing considerable hazards to the natural environment. Since landfill leachates contain a significant amount of toxic inorganic and organic compounds, they cannot be directly introduced to a sewage system [2].

One problem is to find the best way of eliminating landfill leachates. The variation in the leachate composition and volume depends on a number of parameters including season, climate, waste characteristics etc. These make leachate treatment more difficult than other wastewater types [3].

During the initial phase of degradation, landfill leachates are characterized by high concentrations of organics, ammonium, sulfate, chlorides and metals [4]. Many options have been attempted for leachate treatment, with various degrees of efficiency. The most commonly applied methods include several biological and physico-chemical processes [5].

Biological treatments, including anaerobic and aerobic processes, are shown to be quite effective when used in the early stage of leachate production, that is, when BOD_5/COD ratios are high [6]. This ratio generally decreases with increase in the age of the landfill and consequently biological treatments become ineffective [7].

Physico-chemical processes are generally considered to be characterized by higher costs and lower effectiveness [5]. These processes are also mostly used for the treatment of leachates with rather low BOD_5/COD ratios [6].

Recently, there has been increased interest in the use of electrochemical methods for wastewater treatment. Electrochemical methods have been successfully applied to the purification of wastewaters containing phenolic substances [8], refractory organic pollutants [9], cyanides [10], wastewaters generated in textile manufacture [11], tanneries [12] and olive oil production units [13].

In this study a sample of landfill leachate was treated by the application of anodic electrochemical oxidation using a Ti/Pt anode with NaCl as electrolyte. The purpose of this study was to identify the main parameters influencing the performance of an electrochemical oxidation system, the aim being the effective treatment of landfill leachates.

2. Experimental details

2.1. *Experimental procedure*

The parameters that generally influence the performance of an electrochemical oxidation system are the pH and

temperature of the electrolyte, the applied voltage, the type and size of the anode, the input rate of the wastewater to the cell and the type and amount of electrolyte used [14]. It is also reported that the addition of Fe^{2+} ions plays a favourable role through indirect generation of Fenton's reagent [15]. The electrode material plays also an important role in the electrochemical oxidation process. The mechanism and products of some anodic reactions are known to depend on the material of the anode [16, 17].

The parameters investigated are shown in Table 1. These parameters are referred to as the 'controlling parameters' of the system.

The efficiency of the electrolytic system in terms of leachate treatment is expressed though several parameters shown in Table 2. These are referred to as the 'optimization parameters' of the system. 'COD' in the Tables symbolizes the COD removed from the treated leachates.

The effect of the controlling parameters on each optimization parameter was estimated by performing a 2^6 factorial experiment. In general, by using a 2^n factorial design, n controlling parameters interrelate to an optimization parameter though an appropriate linear model. Their significance can also be estimated and assessed [18–20]. Then the most significant variables are altered stepwise, aiming at the determination of the optimal experimental conditions. For the implementation of the 2^6 factorial design, the experimental conditions of the controlling parameters were selected by carrying out preliminary experiments to measure the optimization parameters. These conditions are shown in Table 3.

In the 2^6 factorial design, 64 experiments were carried out. For statistical purposes, four experiments were also performed in the centre of the design (level 0). Each experiment lasted for 5 h. This period was determined to be sufficient for the electrolytic system to achieve steady-state conditions. Every 30 min, a quantity of sample equal to the quantity of wastewater input to the cell in the 30 min period was taken and analysed for COD, BOD_5 and NH_4^+. The mean values of these three analyses were used for further calculations carried out within the analytical procedure. For the determination of these parameters, standard methods of analysis were used [21]. Also, in parallel, the energy consumption of the system was estimated.

Table 1. Controlling parameters of the electrolytic system

Parameter	Symbol
Input rate of wastewater/ml min^{-1}	X_1
Solution pH	X_2
% NaCl used	X_3
Cell temperature/°C	X_4
Applied voltage/V	X_5
$FeSO_4 \cdot 7H_2O$/g l^{-1}	X_6

Table 2. Optimization parameters of the electrolytic system

Parameter	Symbol
% removal of leachate COD	Y_1
% removal of leachate BOD_5	Y_2
% removal of leachate NH_4^+	Y_3
Energy consumption/kWh (kg COD_r)$^{-1}$	Y_4

Table 3. Experimental levels of the controlling parameters for the 2^6 factorial design

Controlling parameter	Variation intervals		
	Level −1	Level 0	Level +1
Input rate/ml min^{-1}	20	40	60
pH	5.5	6.5	7.5
% NaCl	2	3	4
Temperature/°C	60	70	80
Applied voltage/V	20	30	40
$FeSO_4 \cdot 7H_2O$/g l^{-1}	4	6	8

The next step was the estimation of the optimization parameters in infinite electrochemical oxidation time by using a specific analytical method [20]. The linear models of the system were generated using these values.

2.2. *Laboratory pilot plant for the electrochemical oxidation*

The experimental plant is shown in Figure 1. The electrolytic cell was a cylindrical vessel of useful volume 6 L. A Ti/Pt cylindrical electrode (14 cm long × 1.5 cm dia.) was used as anode. The electrode was located inside a perforated stainless steel cylinder (14 cm long × 8 cm dia.) which served as cathode. The pH and cell temperature were adjusted by pH and temperature controllers, respectively. The wastewater input rate to the electrolytic cell was adjusted by a centrifugal pump. The applied voltage was adjusted from a d.c. electrical panel. It must be noted that the range of current densities that were obtained by all experiments was 0.33–0.54 A cm^{-2}. The solution was continuously agitated at a constant rate of 300 rpm.

2.3. *Materials*

The leachate sample used in the experimental procedure was collected from the New Landfill Site of Athens, which started operation in July 1998. The samples were collected in high density polyethylene (HDPE) bottles and were immediately transported to the laboratory in a portable refrigerator, which maintained a constant temperature ($T = 4$ °C). The samples were kept cooled in the laboratory refrigerators at the same temperature. In Table 4 the main characteristics of the leachate used in all experiments are shown. For the determination of these parameters standard methods of analysis were used [21].

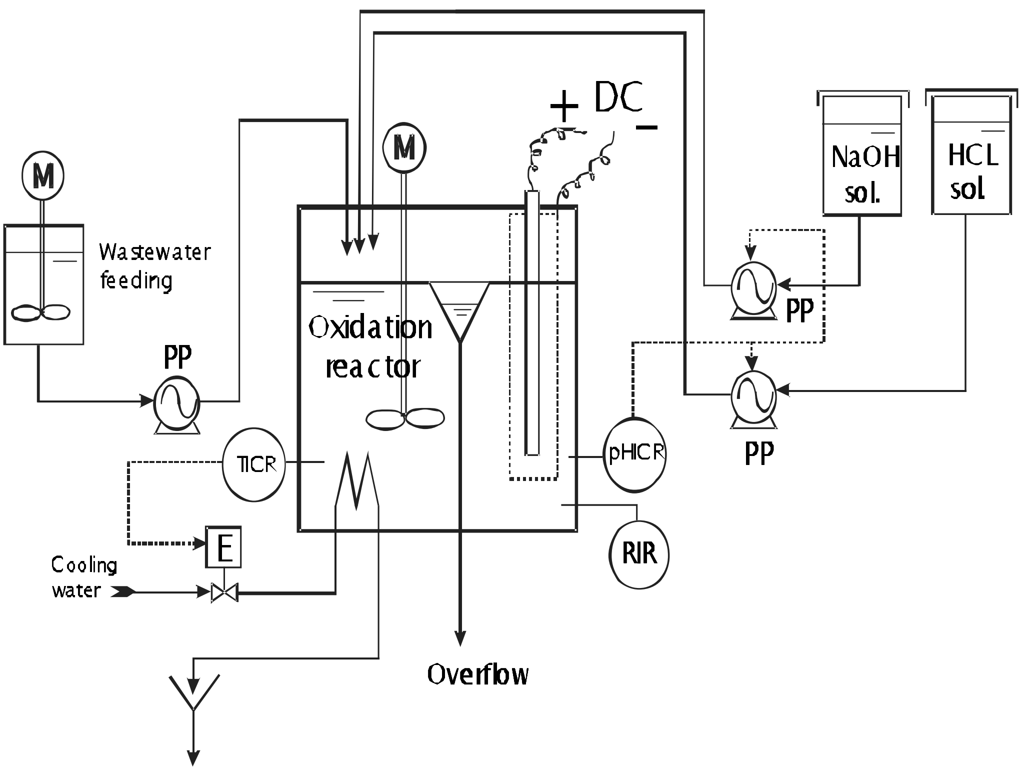

Fig. 1. Experimental plant. Key: (PP) peristaltic pump; (TICR) temperature indicator controller recorder; (pHICR) pH indicator controller recorder; (RIR) redox indicator recorder; (E) electric valve.

3. Results and discussion

3.1. *Linear model for Y_1 (percentage COD removal)*

The estimated linear model interrelating Y_1 with the controlling parameters of the system is the following:

$$Y_1 = 30.82 - 4.32X_1 - 8.93X_2 + 0.002X_3 + 1.83X_4 + 3.19X_5 + 1.10X_6$$

Adequacy of the model: $F_{\mathrm{exp}} = 2.30 < F_{\mathrm{tab}} = 8.57$

The adequacy of the mathematical model derived from the factorial design was validated against the Fisher criterion. More specifically, the Fisher criterion compares the ratio of the square of the variance for adequacy (s^2_{ad}) to the square of the variance for reproducibility (s^2_{y}), called F_{exp}, with the tabulated value F_{tab} for the same degrees of freedom. When the F_{exp} is lower than the F_{tab} the factorial model is adequate; otherwise the model is inadequate [18]. Based on the analysis and the validation process, the linear model generated in these experiments is adequate.

The most significant controlling parameter of the system affecting the percentage COD reduction is the pH in the electrolytic cell (X_2), followed by the input rate of the wastewater (X_1). By decreasing these parameters, the percentage COD reduction is increased. The other controlling parameters are of minor importance. The percentage COD reduction is increased by increasing any of the controlling parameters. The least significant controlling parameter is, by far, the percentage of NaCl (X_3).

In the experimental range studied, the maximum COD removal measured was 53% in the experimental point $(X_1, X_2, X_3, X_4, X_5, X_6) = (20, 5.5, 4, 80, 40, 8)$.

Table 4. Characteristics of leachate used in all experiments

Parameters	Value /mg l^{-1}
pH	6.1
COD	60000
BOD_5	22500
BOD_5/COD	0.375
NH_4^+	1200
Cl^-	3120
P–PO_4	19.6
SO_4^{2-}	510

3.2. *Linear model for Y_2 (percentage BOD_5 removal)*

The estimated linear model interrelating Y_2 with the controlling parameters of the system is the following:

$$Y_2 = 15.89 - 3.31X_1 - 5.84X_2 + 0.2X_3 + 1.34X_4 + 1.71X_5 + 0.66X_6$$

Adequacy of the model: $F_{\mathrm{exp}} = 1.38 < F_{\mathrm{tab}} = 8.57$

The linear model is adequate according to the Fisher criterion and the most significant controlling parameter of the system affecting percentage leachate BOD_5

reduction is the pH in the cell (X_2), followed by the input rate (X_1). The percentage removal of leachates BOD_5 is increased by decreasing these controlling parameters. The other controlling parameters are of minor importance. Percentage BOD_5 reduction is increased by increasing any of the controlling parameters. The least significant controlling parameter is again the percentage NaCl (X_3).

In the experimental range studied the maximum BOD_5 removal measured was 30% in the experimental point $(X_1, X_2, X_3, X_4, X_5, X_6) = (20, 5.5, 4, 80, 40, 8)$. This is the same experimental point on which maximum percentage COD removal was measured.

3.3. *Linear model for Y_3 (percentage NH_4^+ removal)*

In all experiments and for electrolysis time less than 4 h, the percentage removal of leachate NH_4^+ was 100%. As a result there is no need to estimate any linear model for this optimization parameter. Leachates NH_4^+ are totally eliminated in the applied experimental conditions.

3.4. *Linear model for Y_4 (Energy consumption, kWh/kg COD_r)*

The estimated linear model interrelating Y_4 with the controlling parameters of the system is the following:

$$Y_4 = 13.21 - 5.10X_1 + 5.53X_2 - 0.001X_3 - 1.33X_4 + 3.00X_5 - 0.80X_6$$

Adequacy of the model: $F_{\text{exp}} = 6.17 < F_{\text{tab}} = 8.57$

The linear model is adequate according to the Fisher criterion and the most significant controlling parameter affecting the energy consumption of the system in terms of kWh (kg $COD_r)^{-1}$ reduction is the pH in the cell (X_2), followed by the input rate (X_1). The energy consumption of the electrolytic system is decreased by increasing the wastewater input rate and decreasing the pH. The other controlling parameters are of minor importance. Energy consumption is decreased by decreasing the applied voltage (X_5) and by increasing the cell temperature (X_4), the concentration of Fe^{2+} (X_6) and the percentage of NaCl (X_3). The least significant controlling parameter is, by far, the percentage added NaCl.

In the experimental range studied the lower energy consumption measured was 4.29 kWh (kg $COD_r)^{-1}$ in the experimental point $(X_1, X_2, X_3, X_4, X_5, X_6) = (60, 5.5, 4, 80, 20, 4)$.

4. Conclusions

The first important conclusion of the factorial design implemented is that there is no need to develop a linear model for percentage reduction of leachates NH_4^+. In all experiments and for operation times less than 4 h, a 100% NH_4^+ reduction was achieved. Electrochemical oxidation proved to be most effective in the elimination of one of the most important polluting parameters in landfill leachates.

Regarding the reduction of leachate organic load, the results of the factorial design showed a similar performance for COD and BOD_5. According to the estimated linear models, the most prevailing controlling parameters affecting the percentage COD and BOD_5 reduction, were the pH in the cell and the leachate input rate. Furthermore, both parameters can be optimized if lower values of these controlling parameters are implemented in relation to the experimental range used in the factorial design.

For the energy consumption of the system, again, the most important controlling parameters were pH and the leachate input rate. For optimizing energy consumption it is required to lower the pH and increase the leachate input rate.

It was shown that the other controlling parameters are generally of minor importance in all the cases studied. More specifically, the percentage added NaCl was of minor importance. This is probably because the leachate used contained a considerable amount of Cl^-.

Besides the significance of each controlling parameter, the feasibility of altering each parameter in practice must be taken into account. From this point of view the most easily changeable parameter is the input rate of the wastewater, followed by the applied voltage, the concentration of Fe^{2+}, the percentage added NaCl, the cell temperature and the pH. The pH, according to the linear models, is a very significant parameter in all cases, but is difficult to control in practice.

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